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**PYROELECTRIC COMPOUND  
AND METHOD OF ITS PREPARATION**

**FIELD OF THE INVENTION**

This invention relates to pyroelectric compounds, a process for their preparation and devices comprising them.

**5 LIST OF REFERENCES**

The following references are considered to be pertinent for the purpose of understanding the background of the present invention:

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## BACKGROUND OF THE INVENTION

Pyroelectricity is a property of certain crystals consisting of polarization developed in a crystal by an inequality of temperature. Spontaneous or stress-induced polarization, signifying pyroelectricity and piezoelectricity respectively, can appear in ionic solids solely due to a non-centrosymmetrical spatial distribution of ions in a polar crystalline structure. Although theory does not impose strict limitations on the size of a polar crystallite<sup>[1,2]</sup>, the magnitude of pyroelectric and piezoelectric effects of some ceramics, particularly BaTiO<sub>3</sub>, rapidly decrease as grain size diminishes to a few nanometers<sup>[1,3,4]</sup>.

10 Determination of the minimal number of periodically arranged unit cells for which a crystal retains pyroelectric and piezoelectric properties has become increasingly important due to the rapid incorporation of these materials into nanometer-scale devices.

As disclosed in U.S. Patent No. 5,504,330, pyroelectric properties of a thin film made of perovskite materials may be enhanced, by the addition of lead to an original perovskite material having an original ferroelectric critical grain size, and then forming a layer of the lead enhanced perovskite material having an average grain size less than the original ferroelectric critical grain size. The remanent polarization of the layer appeared to be substantially greater than the remanent polarization of the original perovskite material.

20 Thin BaTiO<sub>3</sub> ferroelectric films are important for a number of applications such as high charge density capacitors, ferroelectric memory, and microwave and optoelectronic devices. However, integration of BaTiO<sub>3</sub> into Si microfabrication technology is hindered by the high chemical reactivity of BaTiO<sub>3</sub> with respect to Si. Therefore, despite the small misfit between the lattice parameter of Si and inter-plane distance of BaTiO<sub>3</sub>, epitaxial growth of BaTiO<sub>3</sub> on Si always requires intermediate buffer layers.

DE 10028022 discloses the production of highly ordered low molecular inorganic thin action layers at low temperature on silicon chips in pyroelectric

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detectors. Such production comprises applying an action layer made from a ferroelectric, pyroelectric or piezoelectric material to a substrate with a highly ordered polytetrafluoroethylene coating whereby the action layer is ordered through the polytetrafluoroethylene substrate.

5 It is also known that pyro- and piezo-electric effects may exist in structures that lack the spatial periodicity inherent for ionic crystals, but composed of polar molecules with directional ordering. An example of such a material is a nematic liquid crystal. Spontaneous or stress induced dipole ordering without fine-tuned positional order is theoretically possible in ionic  
10 solids<sup>[5]</sup> as well; however only indirect experimental evidence supporting this theory has been presented so far <sup>[6-9]</sup>.

## SUMMARY OF THE INVENTION

The present invention provides for novel pyroelectric (and consequently  
15 piezoelectric) compound and a method of its preparation.

The compound of the present invention, while being inorganic, shows clear pyroelectric and piezoelectric properties despite the lack of spatial periodicity inherent to ionic crystals.

The inventor has surprisingly found that a quasi-amorphous compound  
20 having a relatively low dielectric constant and a relatively high pyroelectricity may be produced, by subjecting an amorphous compound to a mechanical strain, where the mechanical strain does not promote the formation of crystallites within the quasi-amorphous compound. The compound obtained in the present invention is thus characterized by the advantageous features of amorphous compounds (e.g.,  
25 low dielectric constant, low production costs) and the advantageous features of crystalline compounds (e.g., pyroelectricity and piezoelectricity). The pyroelectric and piezoelectric effects of the quasi-amorphous compound of the invention may be attributed to a spontaneous local dipole ordering, which is usually observed in crystalline solids but not in amorphous ones.

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The term "*quasi amorphous compound*" should be construed herein as a compound which is a non crystalline ionic solid having a macroscopic polarization. The polarization manifests itself as pyroelectric effect.

Thus, according to the first aspect thereof, the present invention provides a  
5 novel pyroelectric compound having an amorphous ionic solid structure with directional polar ordering. More specifically, the present invention provides an inorganic, quasi-amorphous oxide compound of a metal, mixture of metals or semiconducting element, the compound having pyroelectric properties.

According to a preferred embodiment of the invention, the oxide  
10 compound has the formula  $(A_xB_{1-x})_pO_n$ , wherein A and B are independently selected from transition metals, elements of Group IVA of the periodic table, alkali metals, alkali earth metals and rare earth metals; x has values of between 0 to 1; p is an integer having the values 1, 2 or 3; and n is an integer having the value of 1, 2, 3 or 4. Preferably, A is a transition metal or an element of Group IVA of the periodic  
15 table; x is 1 and p is 2. More preferably, the compound is selected from  $SiO_2$  and  $TiO_2$ .

According to another preferred embodiment of the invention, the compound has the formula  $(A_xB_{1-x})(C_yD_{1-y})O_n$  wherein A and B are independently selected from alkali metals, alkali earth metals, rare earth metals and elements of  
20 Group IVA of the periodic table; C and D are independently selected from transition metals and alkali earth metals; x and y have values of between 0 to 1; and n is an integer having a value between 1 to 10. Preferably, n has a value of 1, 2, 3 or 4 and more preferably n is 1, 2 or 3.

According to a preferred embodiment of the invention, A and B are  
25 independently selected from Ba, Sr, Ca, Pb, La, Eu, Li, Na, K and Cs ; C and D are independently selected from Ti, Zr, Nb, Ta, Sc, Mg and V; and n is 3.

Preferably, A and B are independently selected from Ba, Sr, Ca, Pb, La and Eu.

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According to another preferred embodiment, A and B are independently selected from Li, Na, K and Cs.

Similarly, C and D are independently selected from Ti and Zr. According to another preferred embodiment, C and D are independently selected Nb, Ta, Sc, Mg and V.

According to a further preferred embodiment, in the quasi-amorphous compound of the invention,  $y=0$ , thus obtaining a compound of the formula  $(A_xB_{1-x})DO_3$  having pyroelectric properties, wherein A, B, D and x have the meanings defined above.

Specific examples of pyroelectric compounds according to the present invention are  $BaTiO_3$ ,  $CaTiO_3$ ,  $PbTiO_3$ ,  $Pb(ZrTi)O_3$ ,  $Pb(Zr_{0.35}Ti_{0.65})O_3$ ,  $(PbCa)TiO_3$ ,  $(PbLa)(ZrTi)O_3$ ,  $PbLaTiO_3$ ,  $Pb(ScTa)O_3$ ,  $Pb(ScNb)O_3$ ,  $Pb(MgNb)O_3$ ,  $SrTiO_3$ ,  $(Sr_{0.65},Ba_{0.35})TiO_3$ ,  $(Ba_{0.70},Sr_{0.30})TiO_3$  and  $EuTiO_3$ . Preferably, the compound is selected from  $BaTiO_3$ ,  $PbTiO_3$  and  $SrTiO_3$ . More preferably, the compound is  $BaTiO_3$ .

The compound of the present invention has a pyroelectricity in the range from about  $10^{-12}$  C/(cm<sup>2</sup> x K) to about  $10^{-7}$  C/(cm<sup>2</sup> x K).

According to another aspect, the present invention provides a process for preparing pyroelectric compound, comprising applying a mechanical strain to a substantially amorphous compound of the formula  $(A_xB_{1-x})(C_yD_{1-y})O_3$  as defined above, the mechanical strain being such as to prevent crystallization of the compound, thereby obtaining inorganic quasi-amorphous compound having pyroelectric properties. The effect of mechanical strain can be achieved by subjecting the compound to an external field such as a temperature gradient or an electrical field. In a preferred embodiment, the substantially amorphous compound has the formula  $(A_xB_{1-x})DO_3$ , wherein A, B, D and x have the meanings defined above.

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In addition, the present invention provides an inorganic quasi-amorphous compound of the formula  $(A_xB_{1-x})(C_yD_{1-y})O_3$  as defined above, preparable by the process of the present invention.

The present invention according to its yet another aspect provides a device  
5 comprising the compound of the present invention which can be operable as a sensor for sensing external fields including temperature, magnetic and electric field.

The present invention also provides an acoustic wave propagation channel, as well as a birefringent medium, formed by the compound of the present invention.

The compound of the present invention can be formed as a layer coating on  
10 a substrate, which can be any substance of a kind that does not cause a rapid crystallization of the amorphous compound, such as Si, SiO<sub>2</sub> and glass.

## DESCRIPTION OF THE DRAWINGS

In order to understand the invention and to see how it may be carried out in  
15 practice, preferred embodiments will now be described, by way of non-limiting examples only, with reference to the accompanying drawings, in which:

**Fig. 1** is a scheme illustrating the preparation of quasi-amorphous BaTiO<sub>3</sub> films by passing them through a steep unidirectional temperature gradient.

**Fig. 2A** is the X-Ray diffraction spectra of BaTiO<sub>3</sub> films as deposited on  
20 (100) Si (1) in comparison to the spectra of the films passed through the temperature gradient (2) and part of the film (1) heated under isothermal conditions (3). The vertical lines correspond to the standard XRD pattern of tetragonal BaTiO<sub>3</sub> (ICSD Collection Code 23758).

**Fig. 2B** is the transmission electron microscopy (TEM) image and electron  
25 diffraction (ED) pattern of a BaTiO<sub>3</sub> film passed through the temperature gradient.

**Fig. 3A** shows the pyroelectric response of a 182(±10)nm thick amorphous BaTiO<sub>3</sub> film passed through the temperature gradient, to periodic heating by an infra-red laser. The Si substrate is 275µm thick; therefore, constant temperature establishes within about 0.2 msec after the laser switches on and off.



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Fig. 3B shows the temperature dependence of the dielectric constant (at 1 kHz) for amorphous BaTiO<sub>3</sub> thin film; (1) as-deposited film and (2) amorphous film passed through the temperature gradient.

Figs. 4A and 4B show scanning electron microscopy images (secondary electron mode) of, respectively, an amorphous BaTiO<sub>3</sub> thin film passed through the temperature gradient; the other part of the same amorphous films heated in isothermal conditions.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention provides for a novel inorganic non-crystalline oxide compound having pyroelectric and piezoelectric properties, and a method of preparation of this compound.

The method of the present invention comprises subjecting sputtered amorphous compound films to a mechanical strain. This can be implemented by passing the film through a steep temperature gradient. The temperature gradient has to be carefully controlled and to be such as to prevent crystallization of the amorphous compound, thereby obtaining highly stressed amorphous films.

Suitable amorphous compound for use in the process of the present invention may be any compound that possesses piezoelectric and pyroelectric properties in its crystalline form. A specific, non-limiting example of such compound is BaTiO<sub>3</sub>.

In the process of the present invention, a polar ionic solid is produced by alignment of local dipoles of the molecules in an amorphous compound by applying a mechanical strain. Any method that creates a mechanical strain, such as electric field, temperature gradient, etc., would be suitable for achieving alignment of the local dipoles thereby forming a macroscopic dipole moment.

The highly stressed amorphous films obtained by the process of the present invention have pyroelectric and piezoelectric properties as clearly

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demonstrated in the experimental section below. In addition, the obtained films have a low dielectric constant ( $\sim 30$ ) and a cheap producing cost.

Thus, the obtained films represent a polar ionic solid without spatial periodicity and therefore, should be henceforth referred to as quasi-amorphous.

5 Without being bound to theory, a possible mechanism for the formation of polarity in the obtained quasi-amorphous  $\text{BaTiO}_3$  thin films probably includes sharp increase of the dielectric constant during the transformation of the amorphous into the quasi-amorphous films and implies molecular grouping, which is formation of crystal motifs. Crystal motifs earlier observed in electro-  
10 optic glasses can be viewed as regions with a local crystal-like symmetry that gradually vanishes within 2-3 coordination spheres <sup>[15]</sup>.

The steep temperature gradient during formation of the quasi-amorphous films generates a gradient of mechanical strain <sup>[16]</sup> that poles the films due to the flexoelectric effect <sup>[17]</sup>. The strain gradient has two components: in-plane (along  
15 the temperature gradient), and out-of-plane (a result of the clamping caused by the cold part of the film) <sup>[16]</sup>. The latter component is responsible for the out-of-plane orientation of the crystal motifs in the films. Thus, if the crystal motifs are polar, their partial orientation creates a sense of polarity in a quasi-amorphous film as a whole. Once formed, the motifs cannot change their orientation due to  
20 the large in-plane compressive stress <sup>[18,19]</sup>.

A possible mechanism that may provide considerable thermal stability for the obtained quasi-amorphous thin films of  $\text{BaTiO}_3$  is that nucleation of crystalline  $\text{BaTiO}_3$  preferably occurs in a low-density intermediate phase that forms as a result of a large volume expansion of the as-deposited amorphous  
25 phase. Thus, formation of a low-density intermediate phase is seen as a precondition for nucleation and crystallization. In the absence of external mechanical constraints volume expansion is unobstructed and nucleation proceeds freely.

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In a thin film clamped by a substrate, volume expansion is restricted and nucleation may be completely suppressed. This indeed occurs if an as-deposited amorphous film is pulled through a temperature gradient. The obtained quasi-amorphous phase retains thermal stability as long as the mechanical constraints are in place.

According to the mechanism suggested above, two preconditions for the formation and stability of the quasi-amorphous phase are required: a) small enthalpy of crystallization; and b) large volume expansion upon heating prior to crystallization.

Thus as-deposited films of amorphous ionic oxides which satisfy these requirements could potentially form the quasi-amorphous state if pulled through a temperature gradient. Variation of mechanical constraints may produce an indefinitely large number of quasi-amorphous phases with different density.

Combination of strong pyroelectric and piezoelectric effects with low dielectric constant indicates that quasi-amorphous compounds of the present invention are very promising for practical applications. It is important to note that the ratio of pyroelectric coefficient/dielectric constant for quasi-amorphous  $\text{BaTiO}_3$ , as demonstrated in the experimental section is close to or surpasses that of  $\text{LiNbO}_3$ , making it very attractive for pyroelectric detector applications. The compound of the present invention can thus be used as sensor device for sensing an external temperature or electric field to which the compound is exposed, as an acoustic wave propagation channel (being thus useful as a constructional component of a phone device), as a birefringent medium in optical devices, etc.

## EXPERIMENTAL

Reference is now made to Fig. 1 illustrating the preparation of quasi-amorphous  $\text{BaTiO}_3$ . Amorphous 150-250 nm thick  $\text{BaTiO}_3$  layers were deposited by radio frequency (RF) magnetron oxygen plasma sputtering<sup>[20]</sup> on highly conductive (As-doped, 1-5  $\text{m}\Omega\cdot\text{cm}$ ) (100) Si wafers. As-deposited films of  $\text{BaTiO}_3$

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were passed at a rate of 2-5 mm/hr through a narrow (15 mm) hot zone in a vertical furnace with peak temperature of  $T_{\max}=650^{\circ}\text{C}$ . The temperature distribution,  $T$  (in  $^{\circ}\text{C}$ ), as a function of distance,  $x$  (mm), from the hottest point of the zone was adjusted to follow the cubic parabola form:

$$5 \quad T(x) \approx T_{\max} - 0.14|x|^3, \text{ for } |x| < 15 \text{ mm.}$$

For the control experiment, some as-deposited films were heated under isothermal conditions at  $600^{\circ}\text{C}$  for 60 min.

Ellipsometry measurements of the residual layers <sup>[21]</sup> on the Si wafer after  $\text{BaTiO}_3$  was selectively stripped off suggesting that no significant chemical  
 10 reaction between Si and  $\text{BaTiO}_3$  occurred during film deposition and heat treatment.  $\text{BaTiO}_3$  was selectively stripped off with a 15% solution of  $(\text{NH}_3)_2\text{Ce}(\text{NO}_3)_6$ . Silicates and silicon oxide are not soluble in  $(\text{NH}_3)_2\text{Ce}(\text{NO}_3)_6$  and therefore would be easily detected by ellipsometry if formed at the Si/ $\text{BaTiO}_3$  interface. This method cannot distinguish between the oxide grown  
 15 due to the chemical reaction during the heat treatment and the oxide produced by  $(\text{NH}_3)_2\text{Ce}(\text{NO}_3)_6$  (~5 nm) during the film stripping.

As-deposited  $\text{BaTiO}_3$  films were stress-free ( $< \pm 30 \text{ MPa}$ ) with refractive index in the range of  $n_{\perp}=1.97\div 2.02$ , and a very small in-plane-out-of-plane birefringence of  $n_{\parallel}-n_{\perp}=-(0.002\div 0.008)$ , confirming film isotropy. The refractive  
 20 index and birefringence were deduced from ellipsometry with fixed wavelength of  $\lambda=634 \text{ nm}$  at four different incidence angles ( $55\text{-}70^{\circ}$ ).

A compressive stress of  $\sigma_e=2.0\text{-}2.2 \text{ GPa}$  was developed in the films passed through the temperature gradient. The stress was measured by the substrate curvature method <sup>[22]</sup>. The refractive index of these films decreased to  
 25  $n_{\perp}=1.89\div 1.94$  but the birefringence grew to  $n_{\parallel}-n_{\perp}=0.03\div 0.07$ , corroborating the existence of high in-plane compressive stress.

All prepared films were analyzed by X-Ray powder diffraction (XRD, Rigaku corp.  $\text{CuK}_{\alpha}=1.5405 \text{ \AA}$ -2 $\theta$  mode and the pole-figure technique) and by transmission electron microscopy (TEM Phillips CM-120) combined with

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electron diffraction(ED). Scanning electron microscopy (Philips XL30 ESEM-FEG) was employed to image film surfaces and cross sections.

The inventor has further investigated three types of films of the as-deposited amorphous  $\text{BaTiO}_3$ :

- 5        1) dense, smooth and uniform films;
- 2) films with a large number of structural defects and/or large surface roughness; and
- 3) films deposited on a MgO seeding layer.

10        The conclusion of such experiments was that quasi-amorphous state forms preferably if dense, smooth and uniform films are pulled through the temperature gradient.

**Fig. 2A** illustrates the X-Ray diffraction spectra of  $\text{BaTiO}_3$  films as deposited on (100) Si (1) in comparison to the spectra of the films passed through the temperature gradient (2) and part of the film (1) heated under isothermal conditions (3). The vertical lines correspond to the standard XRD pattern of tetragonal  $\text{BaTiO}_3$  (ICSD Collection Code 23758). As shown, X-Ray diffraction (XRD) spectra of the films passed through the temperature gradient are indistinguishable from those of as-deposited films. No XRD peaks apart from those of Si-substrate were observed, indicating the absence of a crystalline phase. The volume detection limit of a crystalline phase by XRD calculated from the signal to noise ratio <sup>[10]</sup> was less than 0.3 %:

**Fig. 2B** shows the transmission electron microscopy (TEM) image and electron diffraction (ED) pattern of a  $\text{BaTiO}_3$  film passed through the temperature gradient. Thus, thorough transmission electron microscopy (TEM) investigation only rarely detected the presence of crystalline grains <sup>[11]</sup> and the concentration of the crystallites estimated from TEM images was far below 0.3%. In contrast to the similarity with respect to electron and X-ray diffraction analysis, as-deposited films and the films passed through the temperature gradient have distinctly different electrical properties.

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Fig. 3A shows the pyroelectric response of a 182(±10)nm thick amorphous BaTiO<sub>3</sub> film passed through the temperature gradient, to periodic heating by an infra-red laser. The Si substrate is 275μm thick; therefore, constant temperature establishes within about 0.2 msec after the laser switches on and off. The films  
 5 passed through the temperature gradient show a large pyroelectric effect  $p_{measured} = (1-3) \times 10^{-9}$  C/(cm<sup>2</sup>×K) (5-15% that of a single crystal of BaTiO<sub>3</sub>), which remains invariable (± 15%) over the temperature range 20-150°C. The time dependence of the electrical current generated by periodical heating has a perfectly symmetric shape, which is a signature for the pyroelectric effect and excludes  
 10 possible misinterpretations.

It should be noted that asymmetric contacts may cause a thin film with a strong dependence of the dielectric constant on temperature to appear pyroelectric. The apparent pyroelectric coefficient of this false pyroelectricity can be related to the contact potential difference,  $D$ , the dielectric constant,  $\epsilon$ , the temperature  
 15 coefficient of the dielectric constant,  $b = 1/\epsilon \times d\epsilon/dT$ , and the film thickness,  $t$ , as  $p = Db\epsilon\epsilon_0/t$ .  $\epsilon_0$  denotes dielectric permittivity of vacuum. For the film under consideration this value is order of  $10^{-12}$  C/(cm<sup>2</sup> K), which is three orders of magnitude below the measured values.

The pyroelectric effect was confirmed independently by the continuous  
 20 temperature ramping technique. The direction of the pyroelectric current indicates that the pyroelectric vector is directed toward the substrate. Application of an external electric field of ±200 kV/cm does not alter the value or the sign of the pyroelectric current, demonstrating that the direction of the pyroelectric vector cannot be changed or reversed (absence of switching).

25 Fig. 3B shows the temperature dependence of the dielectric constant (at 1 kHz) for amorphous BaTiO<sub>3</sub> thin film; (1) as-deposited film and (2) amorphous film passed through the temperature gradient. The dielectric constant was measured by an Alpha dielectric analyzer (Novocontrol Inc.) with sputtered Cr (300nm) top electrodes. The dielectric constant of the films passed through the

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temperature gradient increases monotonically with temperature from  $\approx 30(\pm 3\%)$  at 115 K to  $\approx 31(\pm 4\%)$  at 400 K without discontinuities or abrupt slope changes. The dielectric constant shows only minor variations with frequency ( $< 4.5\%$ ) in the  $1-10^5$  Hz frequency range and the dielectric loss is less than 0.02. As-deposited  
5 BaTiO<sub>3</sub> films do not show any signs of pyroelectricity and have a dielectric constant  $\approx 9^{[12]}$ , with no significant temperature dependence (Fig. 3B).

The films passed through the temperature gradient exhibit a piezoelectric effect of magnitude  $d_{33}=10(\pm 50\%)$  pm/V (5-10% of a single crystal of BaTiO<sub>3</sub>), as measured by the two independent techniques. Pyroelectric and piezoelectric  
10 effects comprising 5-15% of the corresponding values for a single crystal cannot be explained by inclusions of crystallites (less than 0.3%) and thus originate from the highly stressed amorphous phase formed in the films passed through the temperature gradient.

The periodic temperature change technique <sup>[23,24]</sup> with a semiconductor  
15 laser as a heat source <sup>[25]</sup> and a continuous temperature ramping method <sup>[26]</sup> were used to determine the film pyroelectric coefficient. Piezoelectric coefficient was evaluated from Piezoelectric Force Microscopy (PFM) data (MMAFM, DI-VEECO)<sup>[27]</sup>. The measurement was performed using the signal access module to which a sinusoidal voltage was applied to the tip at 5 - 15 kHz, and the resultant  
20 tip response monitored with a lock-in amplifier and by a single path interferometer with a calibrated reference standard (single crystal LiNbO<sub>3</sub>). For the latter, the sample was indium-soldered to a 5mm thick copper plate to avoid substrate bending.

Subjecting the films passed once through the temperature gradient to up to  
25 three such additional cycles did not alter their properties. Isothermal heating (600°C 2 hrs, 680°C 1.5 hrs, 800°C 20 min.) also leaves their properties unchanged. Above 800°C, the BaTiO<sub>3</sub> reacts with Si forming barium silicates<sup>[13]</sup>.

**Figs. 4A and 4B** show scanning electron microscopy images (secondary electron mode) of, respectively, an amorphous BaTiO<sub>3</sub> thin film passed through

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the temperature gradient; the other part of the same amorphous films heated in isothermal conditions. In these experiments, the as-deposited BaTiO<sub>3</sub> films formed polycrystalline BaTiO<sub>3</sub> following isothermal heating for 1 hr at 600°C. The refractive index of these films is quite low  $n_{\perp} = n_{\parallel} = 1.80 \div 1.85$  <sup>[14]</sup> and the  
5 compressive stress of 0.2-0.6 GPa is significantly smaller than that of the films passed through the temperature gradient, as described above. The true pyroelectric effect or stress-induced pyroelectric effect will appear only if the material has no center of symmetry, i.e., the sub-nanocrystalline material has to have an assymetric preferred direction. Thus, the sub-nanocrystalline material  
10 has a local order resulting in appearance of spontaneous polarization. The relatively high thermal stability of the sub-nanocrystalline state and its high birefringence ( $n_{\perp} - n_{\parallel} = -(0.03 \div 0.07)$ ) can be explained by the short-range, stress-induced dipole ordering, similar to what was earlier observed in crystals<sup>28</sup>. Such effects for anisotropic media were considered in the past<sup>29</sup>, however, attempts to  
15 produce a clear pyroelectric signature from a nearly disordered material remained illusive<sup>30</sup>, giving only indirect evidence of the presence of spontaneous polarization. The experiments conducted by the inventor have shown that short-range dipole ordering in the sub-nanocrystalline material is stress-induced and appears during passing the films through the temperature gradient.